DE LA RECHERCHE À L'INDUSTRIE

International Renewable Energy Storage Conference IRES

POWER-TO-GAS PROCESS WITH HIGH TEMPERATURE ELECTROLYSIS AND CO_2 METHANATION

IRES 2013 – Session E1

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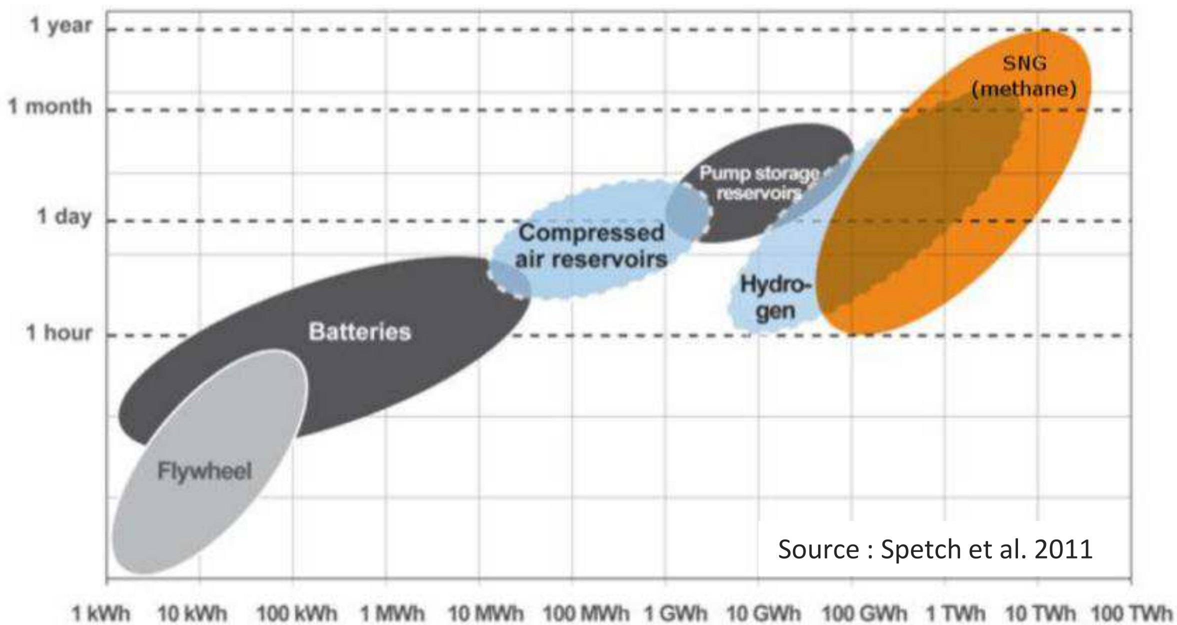
ENERGY BACKGROUND

POWER-TO-SNG : A SOLUTION FOR ELECTRICITY STORAGE

Renewable ressource development : 3 issues for transportation and distribution electrical networks

- High consumption periods
- Excess electric production
- Transportation of energy from production areas to consumption areas

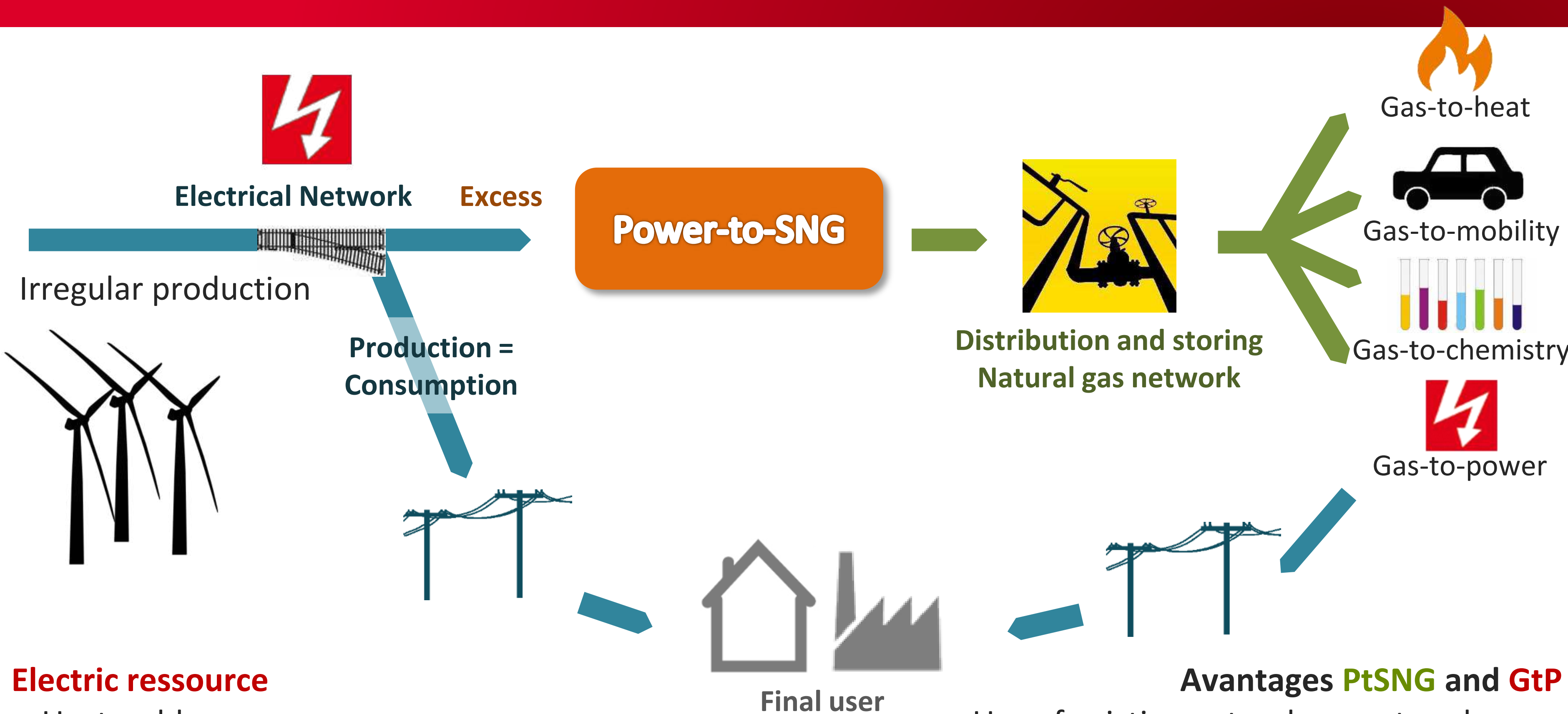


Source : Spetch et al. 2011

SNG

Substitute Natural Gas (methane)

A LINK BETWEEN TWO NETWORKS

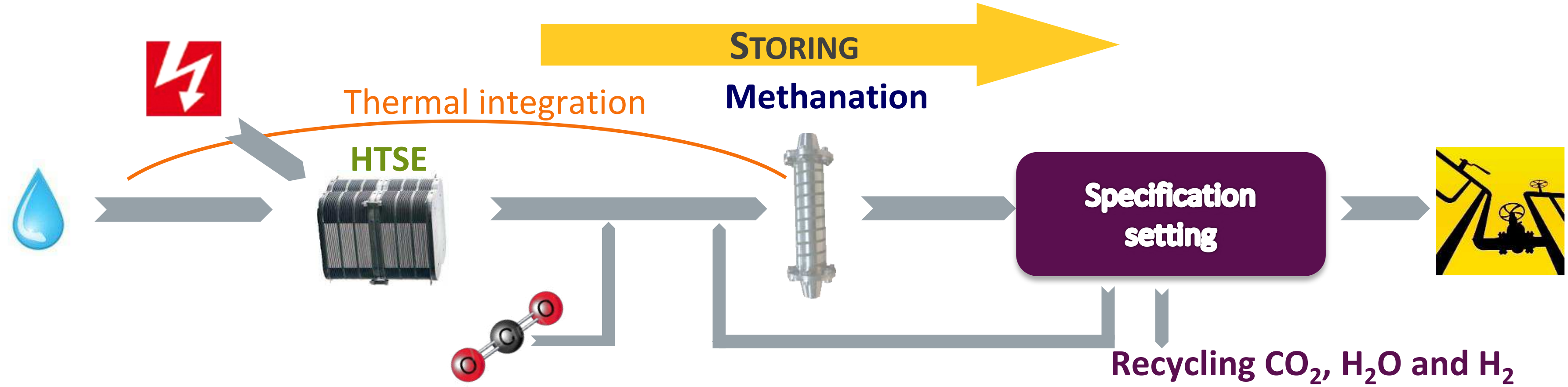


Electric ressource
- Unstorable
- Irregular production
- Network congestion

Avantages PtSNG and GtP
- Use of existing natural gas network
- Mid or long term storage
- Transportation
- Production of electricity
- **Connection of the 2 netwoks**

POWER-TO-SNG PROCESS WITH HIGH TEMPERATURE STEAM ELECTROLYSIS AND CO_2 METHANATION

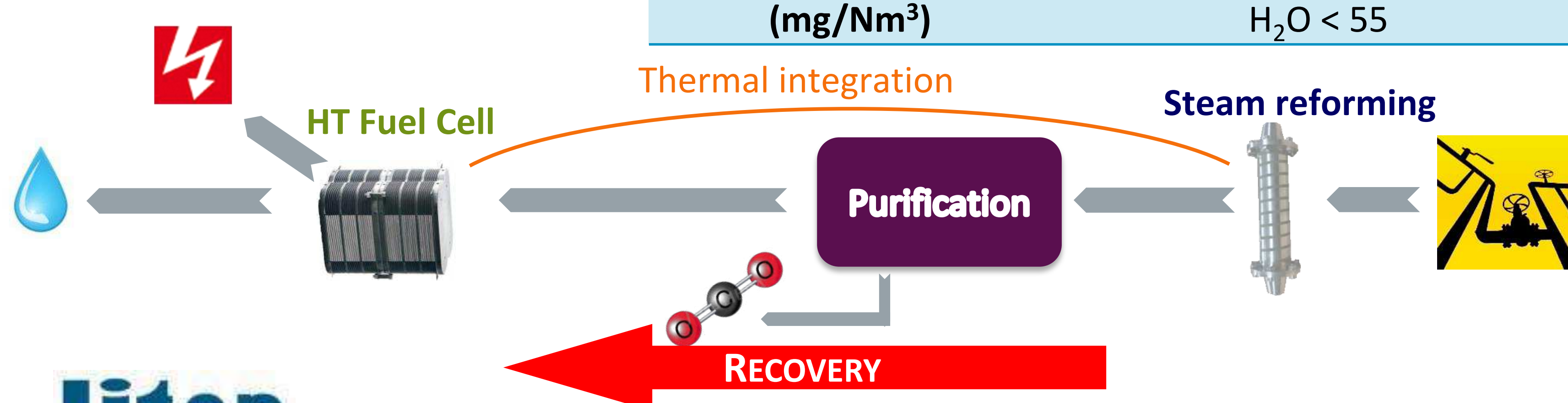
STUDIED POWER-TO-SNG PROCESS ARCHITECTURE



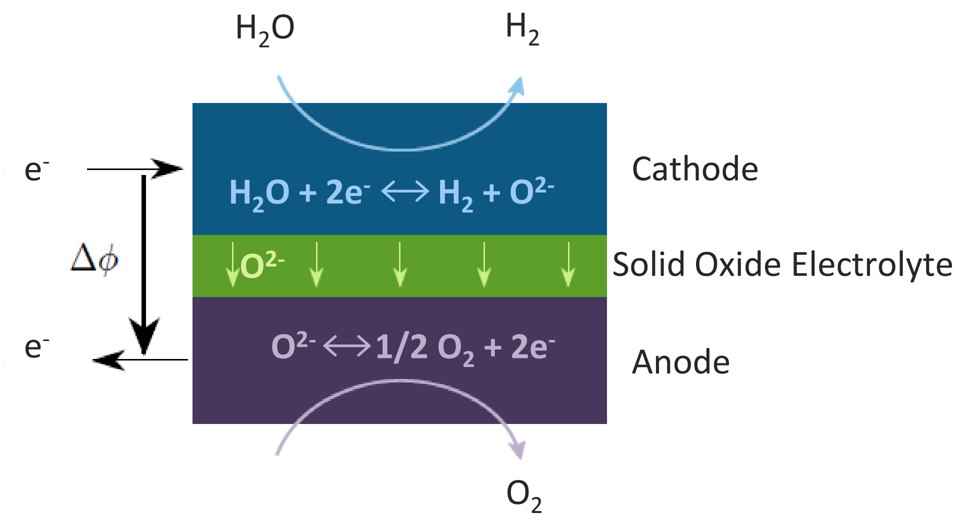
Wobbe index

$$W = \frac{HHV}{\sqrt{\rho}}$$

	NG type H	NG type L
HHV (kWh/Nm³)	10,7 – 12,8	9,5 – 10,5
W (kWh/Nm³)	13,4 – 15,7	11,8 – 13
Composition ($\%_{vol}$)	$CO < 2$, $CO_2 < 3$, $H_2 < 6$	
(mg/Nm³)	$H_2O < 55$	



HIGH TEMPERATURE STEAM ELECTROLYSIS



$$H_2O_{(g)} \leftrightarrow H_2 + ½\ O_2$$

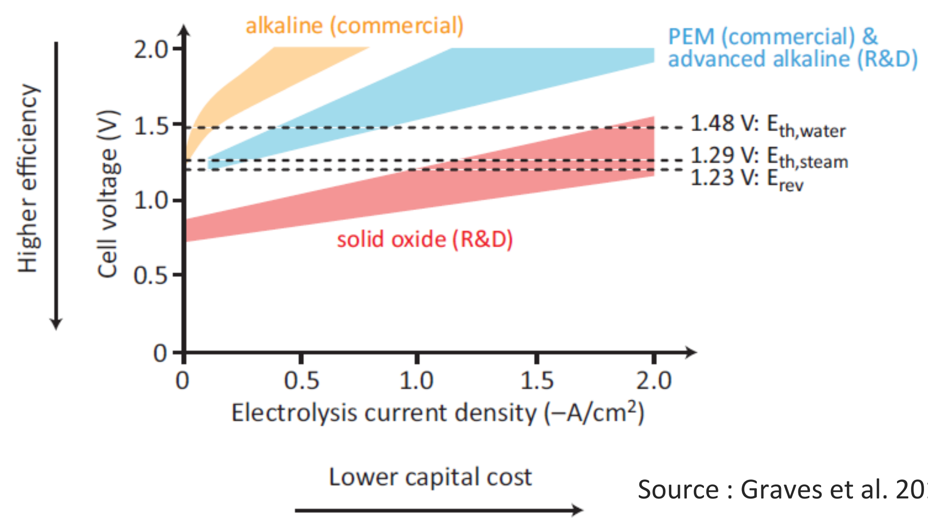
T = 1073 K

HTSE avantages

- High temperature : ΔH decrease
- Irreversibility decrease
- High efficiency
- Reversible (SOEC /SOFC techno)
- Thermal behaviours :
  Exo, auto et endothermal
- Reactants : H_2O and / or CO_2 : co-electrolysis

HTSE current limitations

- R&D
- Cost
- Long-term degradation of performances

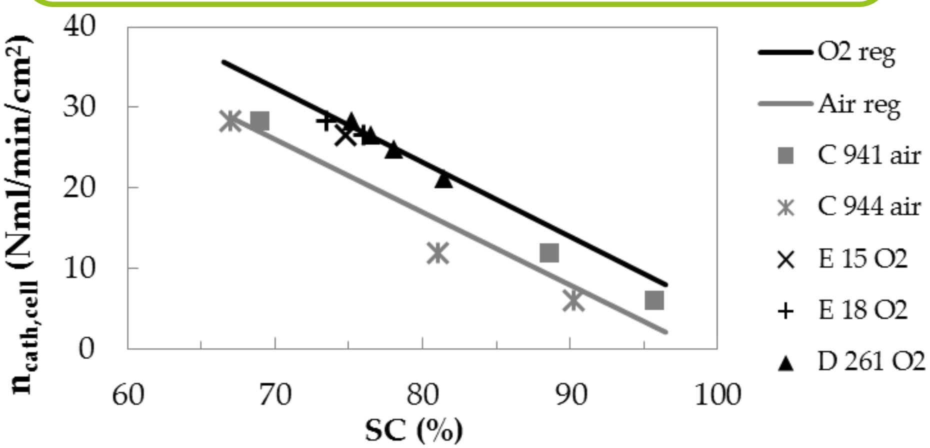


Source : Graves et al. 2011

SIMULATION : HTSE MODELLING AND VALIDATION

HTSE Modelling : To determine P_{elec} and N_{cell} for a incoming flow

- SOEC technology
- $U_{op} = U_{tn}$ and SC : fixed values
- Molar and energy balances : P_{elec}
- Electrochemical modelling : exp. law
- Determination of N_{cell} (and j)
- Correction with pressure and stack effects



Experimental data and interpolated law linking $\dot{n}_{cath,cell}$ and SC for T = 1073 K, P = 1 bar, $U_{op} = U_{tn}$, $H_2 / H_2O = 10 / 90$, on cells referenced C 941, C 944, D 261, E 15 et E 16.

Experimental and phenomenological laws

$\dot{n}_{cath,\ cell} = -0{,}829\ \ SC + 83{,}2$ with air sweep

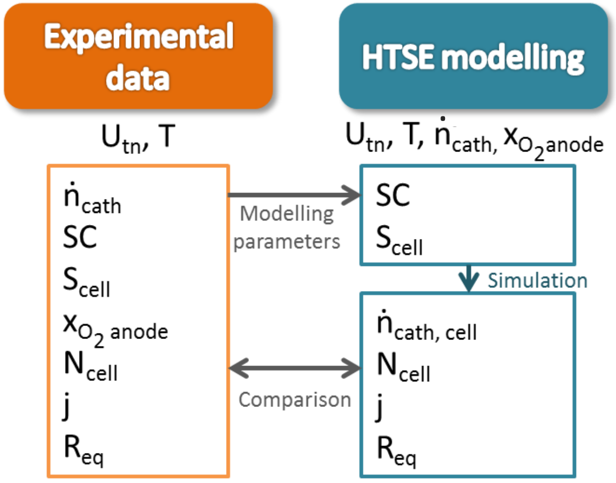
$\dot{n}_{cath,\ cell} = -0{,}727\ \ SC + 81{,}8$ with O_2 sweep

$R_{eq} = (U_{op} - U_{Nernst})/j$ $\Omega.cm^2$

Pressure effect and stack effect

$R_{eq} = R_{eq,\ P°}\ P^{-0{,}09}$ for P [1;10 bar]

$R_{eq,\ Stack} = (R_{eq\ ,cell} + 0{,}034)\ N_{cell}$

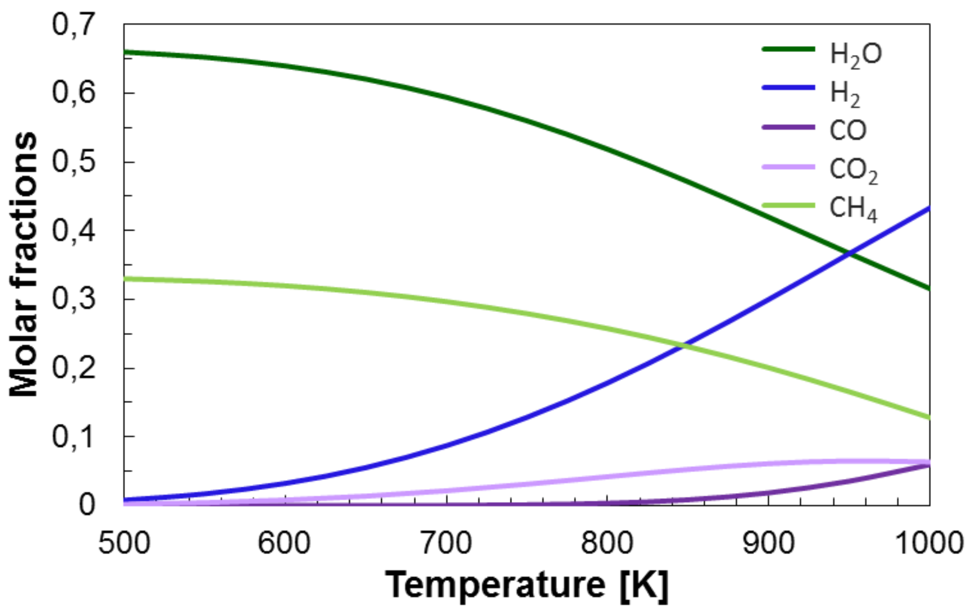


Modelling : Calculation of j and N_{cell} with errors up to 40% → cell dispersion effect

CO_2 METHANATION

Sabatier reaction	**$CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2\,H_2O$**
RWGS reaction	$CO_2 + H_2 \leftrightarrow H_2O + CO$
CO methanation	$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O$
Carbon craking	$CO_2 + 2\,H_2 \leftrightarrow C_{(s)} + 2\,H_2O$

- Catalysed reaction
- Favorable operating conditions for CH_4 production : P ↗ et T ↘



Equilibrum at P = 15 bar for $H_2/CO_2 = 4$

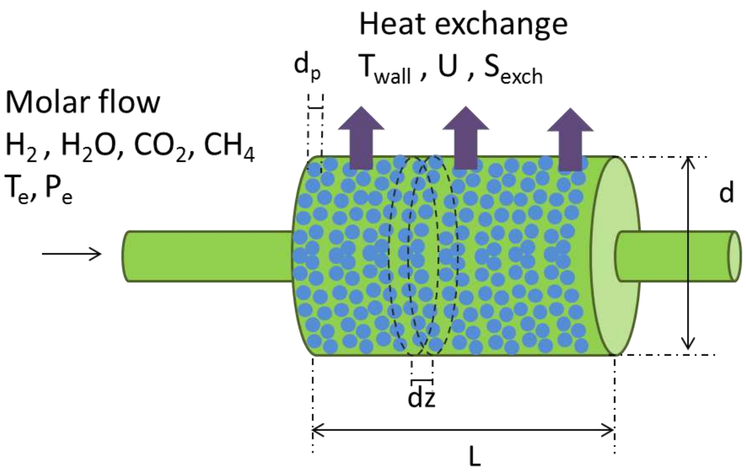
Avantages of CO_2 methanation

- No CO at moderate T
- High CH_4 selectivity
- Exothermal reaction
- High conversion yield
- Existing catalysts

Current limitations of CO_2 methanation

- Poor literature on kinetic laws
- Not a lot of experimental data published, preference given to syngas ($CO + H_2$) methanation

SIMULATION : METHANATION MODELLING



Plug-flow reactor with fixed-bed catalyst and boundary conditions

$$r\left[mol.s^{-1}.m^{-3}\right] = 2691.7.10^{3}\, e^{-64121/RT}\left(P^{n}_{CO_2} P^{4n}_{H_2} - \frac{P^{2n}_{H_2O} P^{n}_{CH_4}}{K_{éq}(T)^{n}}\right)$$

$$K_{eq}(T) = \exp\left(\frac{28183}{T^2} + \frac{17430}{T} - 8.254\ln T + 2.87.10^{-3}\,T + 33.17\right)$$

Pressure (bar)	1	2	30
n	0.225	0.5	1

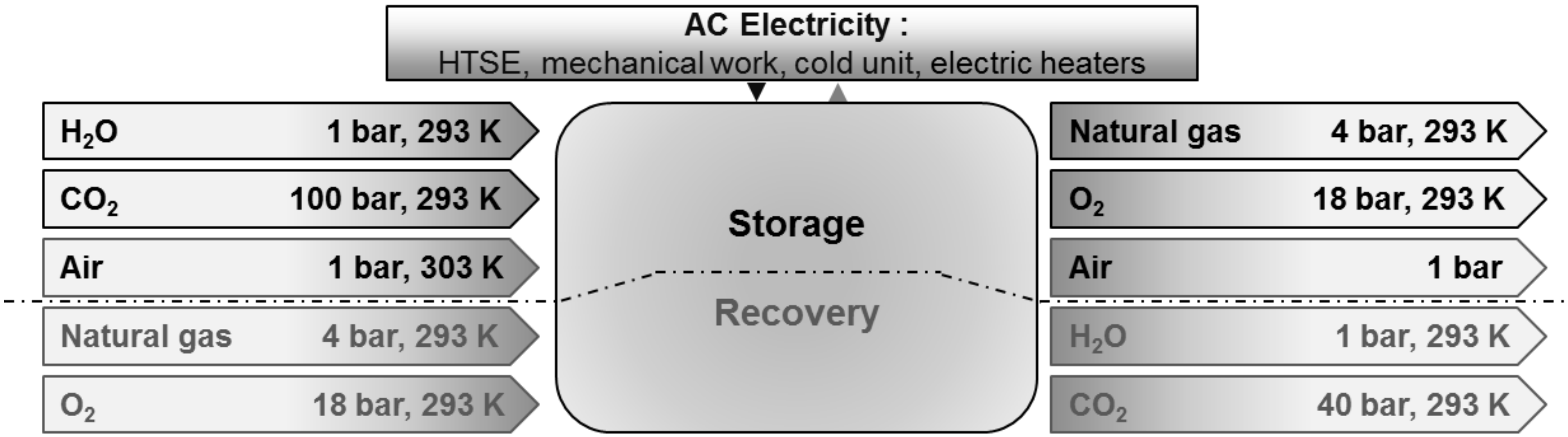
Kinetic law from literature (Cat Ru) [Lunde 1974, Ohya 1997]

Methanation modelling
$CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2\,H_2O$

- 1D plug-flow reactor modelling
- Kinetic law (cat Ru)
- Pressure ≈ 16 bar
- Adiabatic behaviour
- Inlet temperature = 573 K
- Outlet temperature < 973 K

Simulation and experimentation agreement for n = 0.5 (P = 2 bar) for $P_{exp} \in [3.4 ; 7]$
Higher P, lower gap between simulation and experimentation, $\forall$ n used

SIMULATION : PERIMETER AND HYPOTHESES



Pinch analysis module
Process thermal integration

Cold Utility

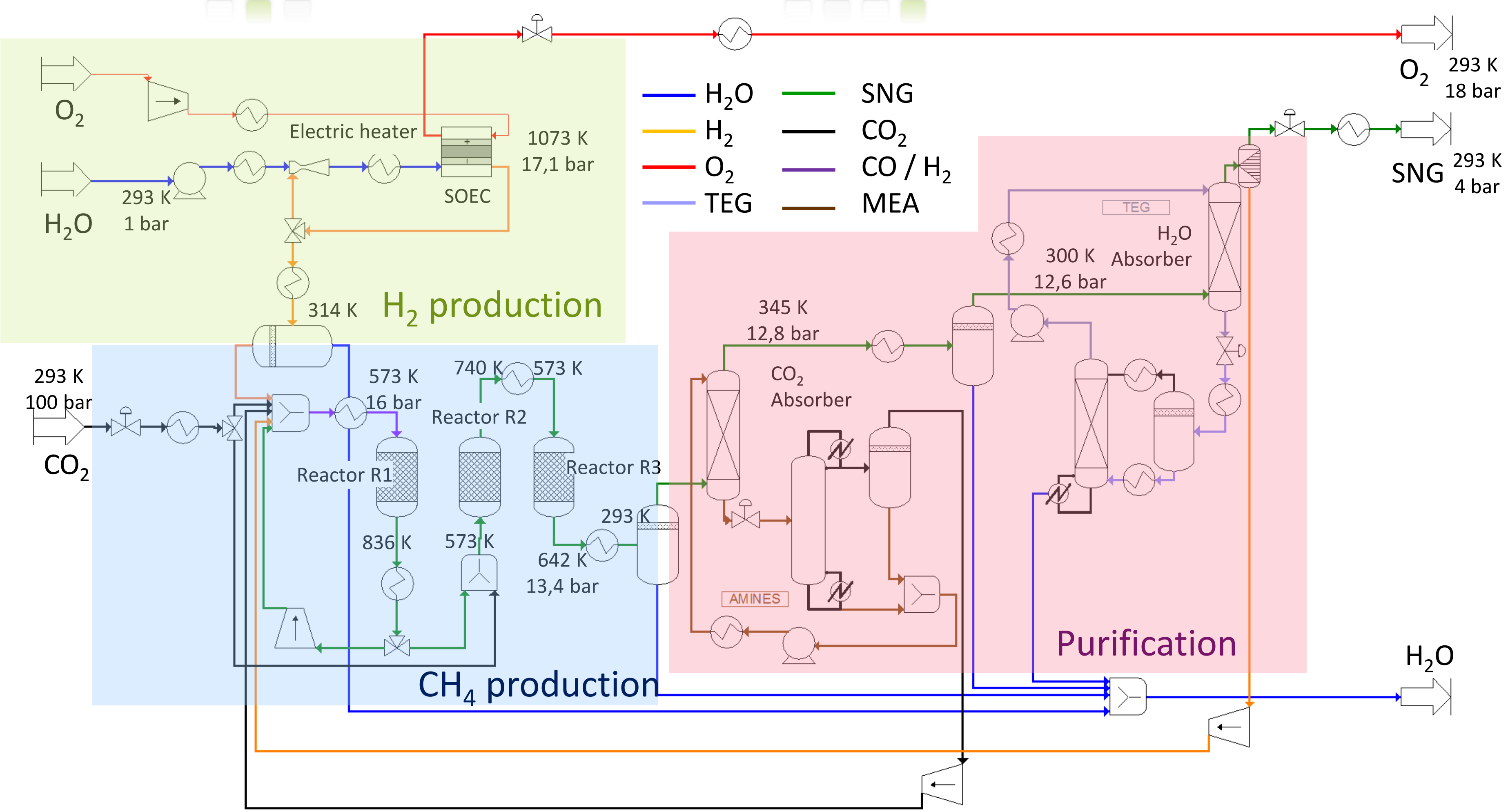
Cold unit (273 K)
$EER_{elec} = 1.73$

Hot Utility

Electric heaters
$\eta = 0.90$

$\eta_{AC/DC} = 0.92$
$\Delta P_{hexch} = 0.2$ bar
$\Delta T_{hexch} = 100\text{-}150$ K

$H_2/H_2O_{HTSE} = 1 / 9$
$H_2/CO_{2\ meth} = 1 / 4$



Energy Efficiency

$$\eta = \frac{\dot{n}_{SNG} HHV_{SNG}}{P_{elec,\,HTSE} + P_{elec,\,mech} + P_{elec,\,hot} + P_{elec,\,cold}}$$

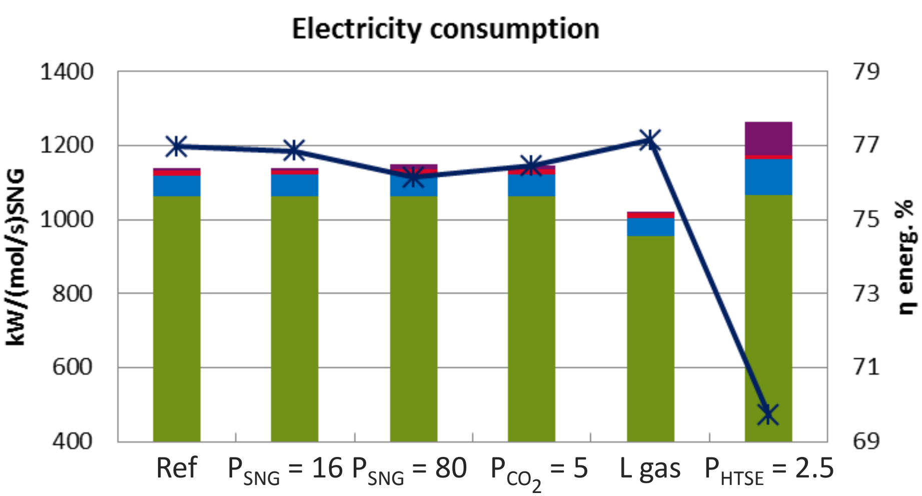
Theorectical Energy Efficiency

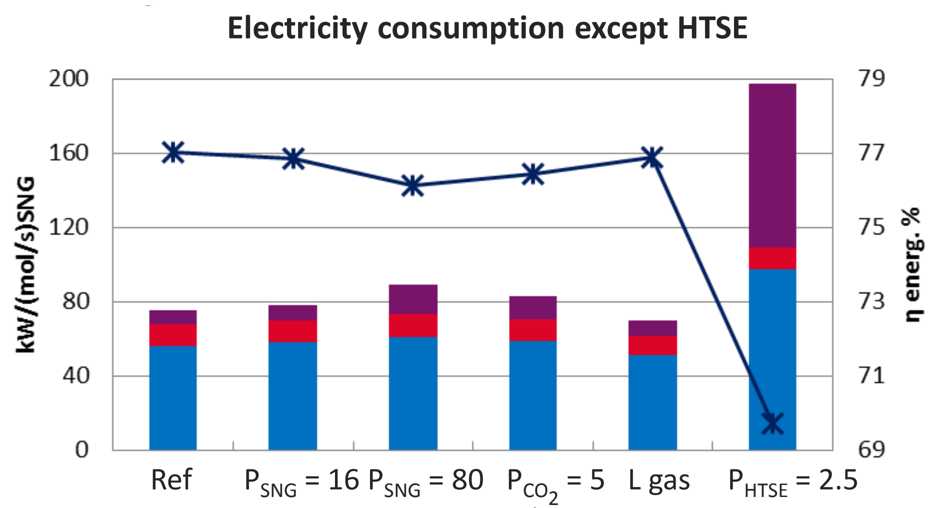
$$\eta = \frac{\dot{n}_{SNG} HHV_{SNG}}{P_{elec,\,HTSE}} = 0.89$$

SIMULATION RESULTS & CONCLUSION

SIMULATION : PARAMETRIC STUDY

$U_{op} = U_{tn}$, SC = 75%, $H_2/CO_2 = 4$, P_{meth} = 16 bar, T_{HTSE} = 1073 K
Reference case : P_{CO_2} = 100 bar P_{SNG} = 4 bar P_{HTSE} = 17 bar H gas
Sensitivity : P_{CO_2} = 5 bar P_{SNG} = 16 and 80 bar P_{HTSE} = 2.5 bar B gas





P_{mech} P_{hot} P_{cold} P_{HTSE} η energ.

- Injection on H or L gas network : no influence on energy efficiency η
- Kind of network (transportation or distribution): high influence on η
- CO_2 origine (separation or storage) : high influence on η
- P_{HTSE} : very high influence on η : loss of 7.4 pts (9.6%) regarding ref. case

$\eta_{HP} \approx$ 77%

$\eta_{LP} \approx$ 70%

CONCLUSION

Modelling

- HTSE modelling for sizing with experimental law
- Adequation between modelling results and experimental data
- Kinetic law and modelling of methanation
- Adequation between simulation results and observed performances
- Scale-up of methanation stage
- Purification of produced SNG

Process simulation

- Production of SNG matching with the specifications
- Two gas qualities (H and L) are achievable
- Higher efficiency if
- The process is operated at high pressure
- CO_2 from industrial storage is used

Thank you for your attention

POWER-TO-GAS PROCESS WITH

HIGH TEMPERATURE ELECTROLYSIS AND METHANATION

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